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14. ABSTRACT Ultrathin polymer films show exceptional property changes that are attributed to the nanoscale confinement of the macromolecules. During the course of the present work (June 2007-August 2011) we have made several discoveries. First, the glass transition temperature can be reduced by over 100 K in the thinnest films we tested and for polycarbonate. This effect, however, is not universal as, for example, poly(vinyl acetate) shows only a weak effect. In addition, we found that the rubbery stiffening of poly(styrene), polycarbonate and poly(vinyl acetate) are					
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Report Title

Final Report: Robust Polymer Films: Nanoscale Stiffening as a Route to Strong Materials

ABSTRACT

Ultrathin polymer films show exceptional property changes that are attributed to the nanoscale confinement of the macromolecules. During the course of the present work (June 2007-August 2011) we have made several discoveries. First, the glass transition temperature can be reduced by over 100 K in the thinnest films we tested and for polycarbonate. This effect, however, is not universal as, for example, poly(vinyl acetate) shows only a weak effect. In addition, we found that the rubbery stiffening of poly(styrene), polycarbonate and poly(vinyl acetate) are similar, with the compliance increasing as the square of the film thickness. However, for poly(n-butyl methacrylate) the response is closer to linear in thickness. Finally, it is also found that the glassy modulus increases by approximately a factor of two-three in the thinnest films.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

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(c) Presentations

Remark ** implies invited presentation.

**G.B. McKenna, "Rheology of Ultrathin Polymer Films: Biaxial Inflation vs. Liquid Dewetting," Society of Rheology Annual Meeting, Cleveland, OH, October 9-13, 2011.

**G.B. McKenna, "Viscoelastic Response of Glass-Forming Liquids: Using Rheology to Probe Glassy Dynamics," Gordon Research Conference on Chemistry and Physics of Liquids, Holderness, NH, July 24-29, 2011.

**G.B. McKenna, "Dynamics of Liquids in Confinement: Small Molecules and Polymer Films," Boston University, Boston, MA, July 23, 2011.

**G.B. McKenna, "Dynamics in Confinement: Consideration of Small Molecules and Polymer Films," Challenges in and Potential of Polymer Physics, Schluchsee, Germany, May 4, 2011.

**G.B. McKenna, "Comportement des Matériaux à l'Echelle Nanométrique: Mesures Thermodynamique et Mécanique," Institut Charles Sadron, Strasbourg, FR, May 2, 2011.

**G.B. McKenna, "Rheological Response of Ultrathin Polymer Films," German Physical Society, Dresden, Germany, March 15, 2011.

**G.B. McKenna, "Deformation and Flow of Matter: Interrogating the Physics of Materials using Rheological Methods," Drexel University, Philadelphia, PA, March 4, 2011.

S.Xu, "Geometry and molecular architecture effects in nanobubble inflation measurements," American Physical Society March Meeting, Dallas, TX, March 23, 2011.

G.B. McKenna, "Rheology of Ultrathin Polymer Films," Annual Meeting of the Society of Rheology, Santa Fe, NM, Oct. 23-29, 2010.

S. Xu, "Nanomechanical Properties of Ultrathin Polymer Films: Measurements on Rectangular vs. Circular Bubbles," Annual Meeting of the Society of Rheology, Santa Fe, NM, Oct. 23-29, 2010.

G.B. McKenna, "Anomalous Mechanical Behavior in Ultrathin Polymer Films," Society of Engineering Sciences Annual Meeting, Ames, IA, Oct. 3, 2010.

**G.B. McKenna, "Thermodynamics and Kinetics of Materials at the Nanoscale," Oklahoma State University, Stillwater, OK, Nov. 30, 2010.

**G.B. McKenna, "Dynamics in ultrathin films," March Meeting of the American Physical Society, Portland, OR, Mar. 15-19, 2010.

**G.B. McKenna, "Dynamics of Glass-forming Systems: Aging Time Dependence and Temperature Dependence," Arizona State University, Tempe, AZ, March 26, 2010.

**G.B. McKenna, "Thermodynamics and Kinetics of Materials at the Nanoscale," Brno University of Technology, Brno, Czech Republic, June 9, 2010.

**G.B. McKenna, "Interrogating the Physics of Materials: Mechanics of Materials from Glass to Rubber and from the Macro to the Nano," 5th International Conference on Times of Polymers and Composites, Ischia, IT, June 20-23, 2010.

**G.B. McKenna, "Structural Recovery in Glasses: Phenomenological Descriptions and Anomalous Behaviors," School on Glass Formers and Glasses, JNCASR, Bengaluru, India, Jan. 4-20, 2010.

**G.B. McKenna, "Comportement des Matériaux à l'Echelle Nanométrique: Mesures Thermodynamiques et Mécaniques," Michelin Centre de Technologies du Ladoux, Clermont-Ferrand, France, July 8, 2010.

**G.B. McKenna, "Solid Rheology of Glass-like Substances," 5th Pacific Rim Rheology Conference, Hokkaido University, Sapporo, Japan, August 1-6, 2010.

****G.B. McKenna, "THE BEHAVIOR OF ULTRATHIN POLYMER FILMS AT THE NANOMETER SIZE SCALE: VISCOELASTIC AND ELASTIC RESPONSES," 6th International Discussion Meeting on Relaxations in Complex Systems, Rome, IT, Aug. 30-Sept. 4, 2009.**

P.A. O'Connell, "Nanomechanical Properties of Ultrathin Polymers," 37th Annual Meeting of the North American Thermal Analysis Society, Lubbock, TX, Sept. 20-23, 2009.

S. Xu, "Unusual Elastic Behavior of Ultrathin Polymer Films and Surface Tension Effects," 37th Annual Meeting of the North American Thermal Analysis Society, Lubbock, TX, Sept. 20-23, 2009.

P.A. O'Connell, "The stiffening of ultrathin polymer films in the rubbery regime – the relative contributions of bending, membrane stress and surface tension," 81st Annual Meeting of the Society of Rheology, Madison, WI, Oct. 18-22, 2009.

****G.B. McKenna, "Interrogating the physics of amorphous solids: Rheological and mechanical measurements," 81st Annual Meeting of the Society of Rheology, Madison, WI, Oct. 18-22, 2009.**

S. Xu, "Molecular stiffening and surface tension in ultrathin polymer films," 81st Annual Meeting of the Society of Rheology, Madison, WI, Oct. 18-22, 2009.

****G.B. McKenna, "Dramatic stiffening in the rubbery plateau regime in ultrathin polymer films," Gordon Research Conference on Elastomers, Networks and Gels, Colby Sawyer College, New London, NH, July, 2007.**

****G.B. McKenna, "Mechanical Behavior of Polymers at the Nanometer Size Scale," Texas Tech University, Department of Mechanical Engineering, Lubbock, TX, September 2007.**

****G.B. McKenna, "Mechanical measurements at the nanometer size scale: Why and what do we learn?" Fowler Distinguished Lecturer, Texas A&M University, College Station, TX, November 2007.**

G.B. McKenna, "The viscoelastic properties of ultrathin polymer films as measured with a novel nanobubble inflation technique." March Meeting of the American Physical Society, New Orleans, LA, March 2008.

****G.B. McKenna, "Viscoelastic properties of ultrathin polymer films and polymer surfaces: Novel nanometer scale measurements," California Institute of Technology, Pasadena, CA, April, 2008.**

****G.B. McKenna, "Mechanical measurements at the nanometer size scale: Why and what do we learn?" Massachusetts Institute of Technology, Cambridge, MA, April 2008.**

****G.B. McKenna, "Viscoelastic response of Ultrathin Polymer Films and Surfaces: Is there a liquid layer?" Mechanics of Time Dependent Materials 2008 Conference, Monterey, CA, April 2008.**

G.B. McKenna, "Time-temperature and time-thickness superposition in ultrathin polymer films," XVth International Congress on Rheology, Monterey, CA, August 2008.

****G.B. McKenna, "Melt State Stiffening in Ultrathin Thermoplastic Films," North American Thermal Analysis Society 36th Annual Conference, Atlanta, GA, August 2008.**

****G.B. McKenna, "Nanomechanics in Polymers: Ultrathin Films and Surface Viscoelasticity," University of Colorado, Boulder, CO, October, 2008.**

****G.B. McKenna, "Characterization of Organic Materials at the Nanometer Size Scale: Mechanical and Thermal Properties," Sandia National Laboratories, Albuquerque, NM, October 2008.**

G.B. McKenna, "Unusual elastic behavior of polymer thin films and surface tension effect," Annual Meeting of the American Physical Society, Pittsburgh, PA, March, 2009.

G.B. McKenna, "The stiffening of ultrathin polymer films in the rubbery regime: the relative contributions of bending, membrane stress and surface tension," Annual Meeting of the American Physical Society, Pittsburgh, PA, March, 2009.

**G.B. McKenna, "Microbubble Inflation measurements of the mechanical response of ultrathin films: viscoelasticity, rubbery stiffening and surface tension effects," Deformation, Yield and Fracture of Polymers, Rolduc Abbey, Kirkrade, The Netherlands, April, 2009.

**G.B. McKenna, "Material Behavior at the Nano-scale: Thermodynamic and Dynamic Considerations," Notre Dame University, South Bend, IN, April, 2009.

**G.B. McKenna, "Comportement des materiaux a l'echelle nanometrique," Arts et Metiers-Paristech, Paris, France, June, 2009.

**G.B. McKenna, "Tg, Aging and Viscoelasticity at the Nanoscale," Roskilde University, Summer School on Aging of Slowly Relaxing Systems,Søminestationen, Holbæk, Denmark, June, 2009.

**G.B. McKenna, "Mechanical Measurements at the Nanometer Size-Scale: Freely Standing Films and Surfaces," Ben Gurion University of the Negev,Beer-Sheeva, Israel, July, 2009.

Number of Presentations: 41.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
10/17/2011	7.00 Gregory B. McKenna, Paul A. O'Connell, Shanhong Xu, Jinhua Wang. Rheological Response of Ultrathin Polymer Films, Proceedings, 242nd American Chemical Society National Meeting and Exposition,Denver, CO, August 28-September 1, 2011.. 2011/08/28 01:00:00, . : ,
TOTAL:	1

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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10/17/2011	10.00	Shanhong Xu, Paul A. O'Connell , Gregory B. McKenna. Nanomechanical measurements in ultrathin polymer films: Rectangular "bubble" inflation measurements, ANTEC 2008 ---- 66th Annual Technical Conference & Exhibition, Milwaukee, WI, May 4---8. Society of Plastics Engineers (2008). 2008/05/04 01:00:00, . : ,
10/17/2011	8.00	Paul A. O'Connell , Gregory B. McKenna. Nanomechanical measurements in ultrathin polymer films, ANTEC 2010 --68th Annual Technical Conference & Exhibition, Orlando, FL, June 16---20. Society of Plastics Engineers.. 2010/06/16 01:00:00, . : ,
10/17/2011	9.00	Shanhong Xu, Paul A. O'Connell , Gregory B. McKenna. Nanomechanical properties in ultrathin polymer films: measurement on rectangular vs circular bubbles, ANTEC 2010 --68th Annual Technical Conference & Exhibition, Orlando, FL, June 16--20. Society of Plastics Engineers (2010). 2010/06/16 01:00:00, . : ,
TOTAL:		3

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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10/18/2011	12.00	S. Xu, P.A. O'Connell, G.B. McKenna , S. Castagnet. Nanomechanical properties in ultrathin polymer films: Measurement on rectangular vs circular bubbles, Journal of Polymer Science Part B: Polymer Physics (09 2011)
TOTAL:		1

Number of Manuscripts:

Books

<u>Received</u>	<u>Paper</u>
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TOTAL:

Patents Submitted

Patents Awarded

Awards

1. Received the 2009 Bingham Medal of the Society of Rheology. October 20, 2009.
 2. Appointed Michelin Chair at the E.S.P.C.I. in Paris, FR. July, 2010.
-

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Shanhong XU	0.65	
FTE Equivalent:	0.65	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Gregory B. McKenna	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Shanhong XU

Total Number:

1

Names of other research staff

NAME

Paul A. O'Connell

FTE Equivalent:

Total Number:

PERCENT SUPPORTED

0.69

0.69

1

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Final Report for Agreement Number W911NF-07-1-0418 “Robust Polymer Films: Nanoscale Stiffening as a Route to Strong Materials.”

Principal Investigator: Gregory B. McKenna, Department of Chemical Engineering
Texas Tech University, Lubbock, TX 79409-3121

Report for Period June 26, 2007 – June 25, 2011

Introduction

The present document forms the narrative of our accomplishments on the project “Robust Polymer Films: Nanoscale Stiffening as a Route to Strong Materials.” The work in the project focused on the mechanical response of ultrathin polymer films using the Texas Tech nanobubble inflation technique as the means to determine the viscoelastic properties of films as thin as 3 nm. In the course of the work, we were able to demonstrate that the extreme stiffening observed in the rubbery plateau regime of polymers is not caused by the surface tension in the films. In addition, we discovered the first evidence of flow in the nanobubble inflation experiments when we were able to work below 10 nm thickness in polycarbonate. These latter experiments also showed the exceptional property change that the glass transition temperature in a 3nm thick polycarbonate film is reduced to below room temperature from the macroscopic value of approximately 136 °C. This is, at present, the largest reduction in the glass transition ever seen in an ultrathin polymer film.

Experimental Methods

Materials

We have worked with four materials in the course of the present project: polystyrene, poly(vinyl acetate), poly(*n*-butyl methacrylate) and polycarbonate. The properties of the studied materials are shown in Table 1. In addition, we have made preliminary measurements on a star-branched polystyrene whose properties are also given in Table 1.

Table 1. Molecular weights and T_g s of the polymers investigated.

Polymer	M_w(g/mol)	M_w/M_n	T_g (°C)
Poly(vinyl acetate)	157,000	2.79	30.6
Linear Polystyrene	994,000	1.07	98.8
3-arm, star-branched polystyrene	352,000	1.07	98.0
Linear Polycarbonate	47,000	2.55	136.9
Poly(<i>n</i> -butyl methacrylate)	179,000	2.4	20.2

The Nanobubble Inflation Method

The details of the TTU nanobubble inflation method are given elsewhere^{1,2}. The essentials of the method are that an extremely thin polymer membrane is created by spin coating onto a smooth surface, generally mica. The film is then lifted off of the mica by floating onto a water surface where it can be picked up by a template that contains micron dimensioned through channels. In most of our work we have used circular channels, which then give an equibiaxial bubble inflation test method. We have also used rectangular bubbles for the purpose of establishing that the geometry of the deformation is not an important contributor to the observed results. Figure 1 shows a typical array of inflated bubbles and Figure 2 shows the increase in

bubble height as time progresses. It is this time-progression of the bubble profile or shape that permits the determination of the viscoelastic response of the ultrathin polymer films¹⁻⁴.

In most of our work we used the nanobubble inflation test to inflate circular bubbles. In the work upon which we report here we also carried out experiments on rectangular bubbles in order to establish whether or not the geometry of deformation (equibiaxial vs. plane strain) would significantly alter the results. This is discussed in the appropriate section.

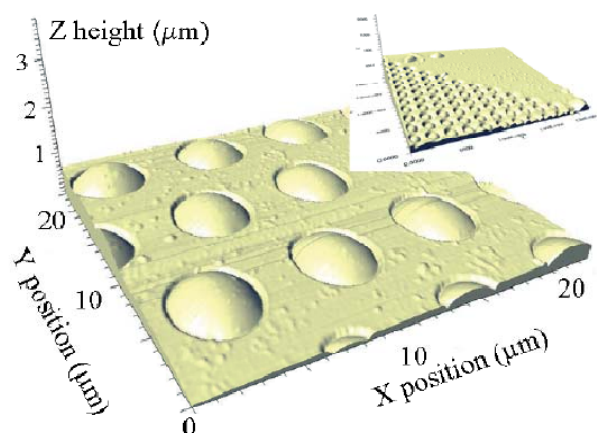


Figure 1. Three-dimensional AFM image of inflated bubbles. The scan area is approximately $23 \times 23 \mu\text{m}$ on a template containing $5 \mu\text{m}$ diameter holes. The image is of a PVAc film at a thickness of 150 nm , a pressure of 34.5 kPa and at a temperature of 40°C . The inset shows a similar scan area with inflated bubbles over $1.2 \mu\text{m}$ holes. (After ref. 4)

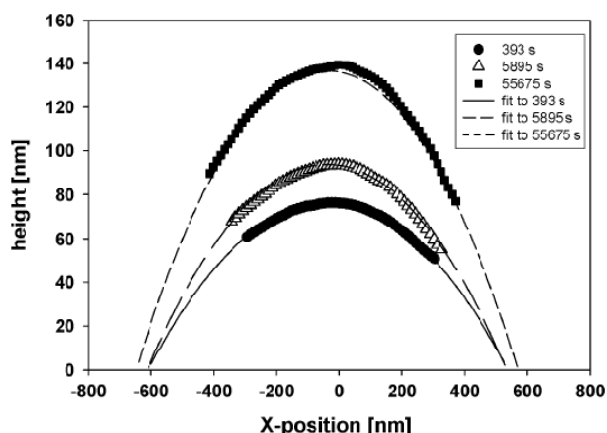


Figure 2. The center-line profile plots for a 23 nm thick polystyrene (PS) film at 55°C and a pressure of 124 kPa . Filled circle, open triangle and filled square are at 393 , $5,895$ and $55,675 \text{ s}$, respectively. (After ref. 4).

Results

Biaxial Bubble Inflation: Thermoviscoelasticity

The viscoelastic responses of polystyrene (PS), polyvinyl acetate (PVAc) and polycarbonate (PC) were all considered as was the response of a star-branched polystyrene. Figure 3 shows the master curve construction of the creep vs. reduced time for the polystyrene material for different film thicknesses. The reference temperature for each of the thicknesses is taken as the apparent glass transition temperature. There are three things to be noted from this figure. First, the creep response goes from the glassy regime through a segmental dispersion and onto a “rubbery-like” plateau. This is expected, but the magnitude of the rubbery plateau is not constant and independent of film thickness, rather there seems to be dramatic stiffening, which we return to subsequently. The second thing to observe is that the reference temperatures decrease as film thickness decrease. This is consistent with the behavior reported in “pseudo-thermodynamic”⁵ measurements where the break in a plot of, e.g., film thickness vs. temperature is taken to be the glass transition temperature, and where T_g has been observed to decrease significantly^{6,7}. In the case of poly(vinyl acetate) we observed no change in the T_g , though the rubbery stiffening was observed. For the polycarbonate, we observe even greater reductions in the glass transition temperature than we did for the polystyrene. Figure 4 shows the three materials compared. It is clear that the PVAc shows little change in T_g while the PS and PC both show significant changes. The truly exceptional change is that for the PC films

where thicknesses below 5 nm could be obtained and the T_g reduction is well over 100 °C. This is particularly surprising as the PS has a molecular weight close to 10^6 g/mol while that of the PC is less than 5×10^4 g/mol and the greatest changes in T_g reported previously were for the highest molecular weight PS materials⁷. This is an area that clearly merits further investigation. Finally, both the PS and the PC show significant stiffening in the glassy regime. This is evident in Figure 3 for the PS and similar results were obtained for the PC. Again, this is an important finding and merits further investigation.

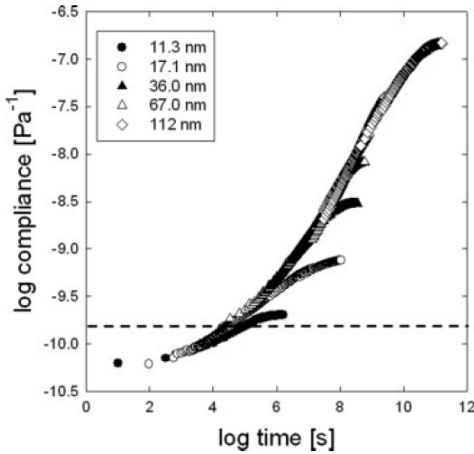


Figure 3. Time-temperature master curves for PS For film thicknesses of 11.3 nm ($T_{ref}=39$ °C), 17.1 nm ($T_{ref}=48$ °C), 36.0 nm ($T_{ref}=69$ °C), 67.0 nm ($T_{ref}=85$ °C), and 112 nm ($T_{ref}=95$ °C). The dashed line represents the macroscopic glassy compliance. (After ref. 3).

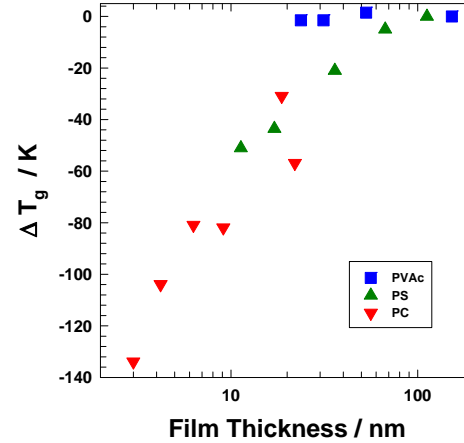


Figure 4. Glass transition temperatures for ultrathin films of poly(vinyl acetate), polystyrene and polycarbonate. (After ref. 8).

Biaxial Bubble Inflation: Rubber Stiffening

The large rubbery stiffening observed in the ultrathin films is surprising and, at this point in time, remains unexplained. During the present project we undertook two endeavors to further explore this phenomenon. First, we looked at two different materials that had not previously been

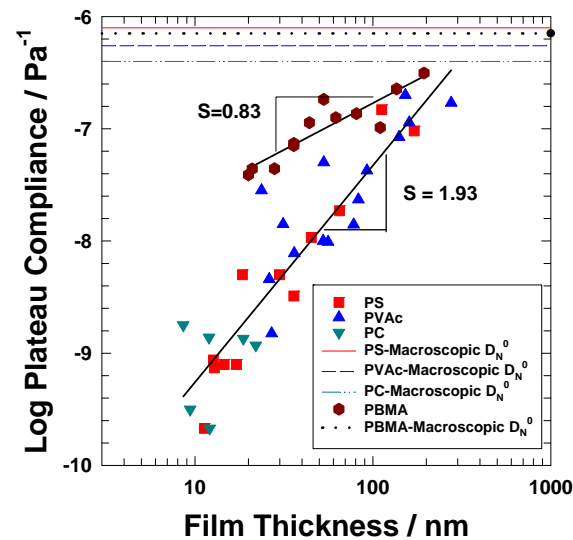


Figure 5. Comparison of the rubbery plateau compliance as a function of film thickness for PVAc, PC, PS, and PBMA. (After ref. 8).

investigated, poly(*n*-butyl methacrylate) (PBMA) and polycarbonate (PC). In this context it is important to remind the reader that in our earlier work^{1,9} we had seen dramatic stiffening in both PVAc and PS and the stiffening was such that the rubbery compliance scaled approximately as the thickness squared. In the case of the polycarbonate we found that the rubbery plateau in the thinnest films for which we could test the rubbery stiffness fell essentially on the extrapolated behavior from the PS and PVAc data of compliance vs. film thickness. However, in our experiments, we found that the PBMA did not follow this behavior. Although the PBMA did exhibit significant stiffening as the films became thinner, the effect was less significant, following a weaker power law dependence on thickness than

in the other three materials. A comparison of the four different materials is given in Figure 5.

Another aspect of the rubber stiffening in these materials is the possibility that the stiffening is due to surface tension contributions¹⁰. We spent considerable effort showing that this is not the case. In addition to showing that the surface tension is not the primary cause of the observed stiffening, we also showed that the bubble inflation measurements can be used to determine the surface energy of the ultrathin films. These results were shown in references 9,12,12.

Plane Strain Bubble Inflation

Because the results of the biaxial bubble inflation measurement were so striking, we determined that it would be of interest to make measurements in a different geometry of deformation, and we now describe those results. In the specific instance, we decided to carry out measurements using a slotted geometry that was $800\text{ nm} \times 2.6\text{ }\mu\text{m}$ on templates similar to the circular geometry bubbles. The difficulty of the results lay in the need to consider the full problem of bending and membrane inflation because the films generally ruptured before the membrane limits could be achieved. In spite of this, we were able to make inflation measurements and analyze them (with help from Dr. Sylvie Castagnet at the Ecole Nationale Supérieure d'Aéronautique et Mécanique in France) using a finite element program. Figure 6 shows the slotted template as imaged by AFM. Figure 7 shows a plot of the line profiles across a rectangular bubble.

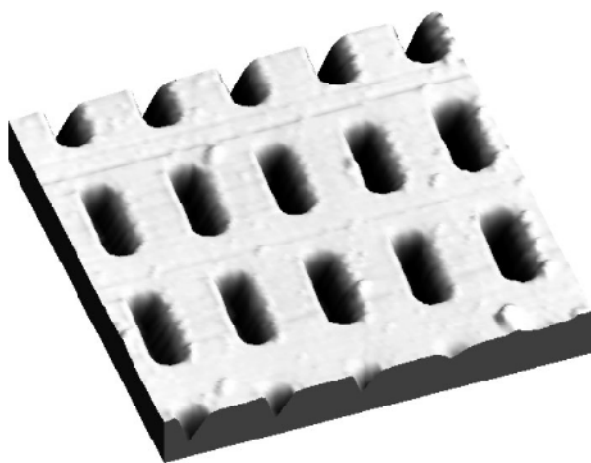


Figure 6. Three-dimensional AFM image of a substrate containing $0.8\text{ }\mu\text{m} \times 2.6\text{ }\mu\text{m}$ slots. (After ref.13,14).

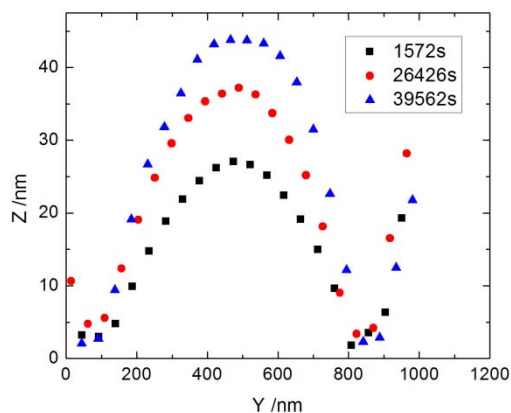


Figure 7. Line profiles along the width in the center of the rectangular bubble at different times for a 30 nm thick PS film supported over a rectangular slot. $T=84\text{ }^{\circ}\text{C}$. (After ref.13,14).

The results of comparing polystyrene inflated as a rectangle and inflated as a circular membrane shows that the differences are minor. As seen from the master curve comparison of Figure 8 there is a slight shift in time and a possibly greater rubbery stiffness in the rectangular bubble when compared with the circular bubble. However, these differences are within the experimental variability. Furthermore, of considerable interest is the observation that the rectangular bubble has a similarly reduced glass transition temperature as does the circular bubble. These comparisons are shown in Figures 9 and 10.

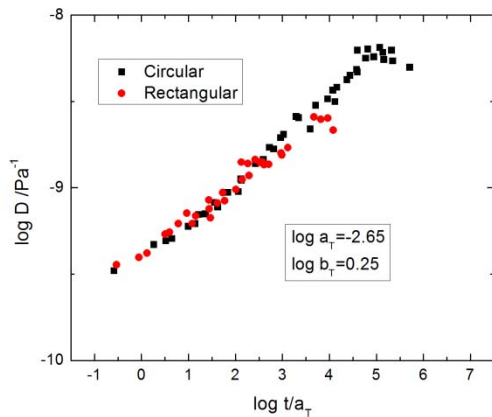


Figure 8. Master curves for creep of PS nanobubbles having rectangular and circular shapes. The circular membrane had a thickness of 24 nm and the rectangular membrane had a thickness of 30 nm. (After ref.13, 14.).

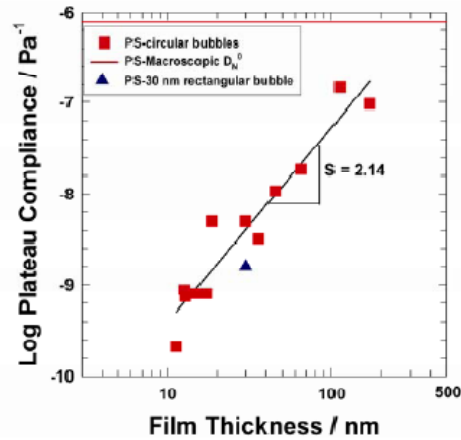


Figure 9. Log plateau compliance vs. film thickness showing that rectangular bubble compliance is similar to that of the circular bubble results. (After ref.13,14.).

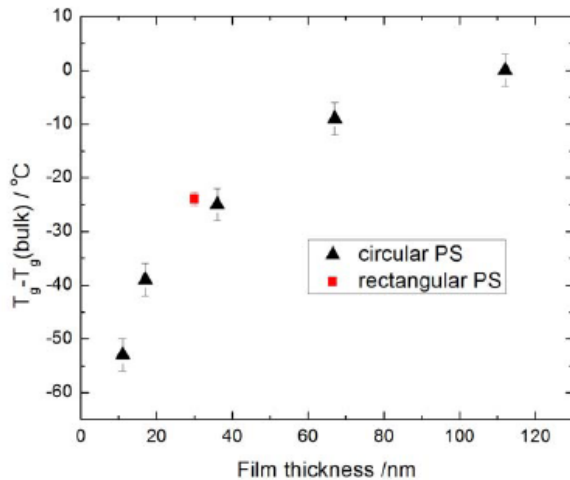


Figure 10. T_g reduction vs. film thickness for circular and rectangular PS bubbles. (After ref. 13,14.).

Star-branched Polystyrene

The current investigation of the viscoelastic response of ultrathin polymer films was climaxed by a brief set of experiments to investigate the impact of molecular architecture on the response of the thin film response in the biaxial (circular membrane) bubble inflation method. A three-armed star polystyrene of branch molecular weight $M_n=109,800$ g/mol and $PDI=1.07$ was used in the study (see Table 1). Films were spin cast and floated onto templates with 5 μm diameter channels and tested in a fashion similar to the linear polystyrene described previously. The star-branched PS films tested had thicknesses of 14, 19 and 28 nm. Figure 11 shows the creep responses at different temperatures for the 28 nm film. We remark that the

temperatures of creep are clearly below the macroscopic T_g value for this polystyrene (98 °C). Time-temperature superposition was applied to the data for all three film thicknesses and the shifting was used to determine the glass transition temperatures for the films. Figure 12 shows the T_g reduction of the three star-branched polystyrene film thicknesses and compares them with the linear polystyrene. As we see, the T_g reductions are very similar. This is somewhat surprising because the T_g reduction in ultrathin freely standing films of polystyrene has been reported to be dependent on the molecular weight^{6,7} above a molecular weight of approximately 350,000 g/mol. Hence, one might have expected that the star-branched polystyrene having a total molecular weight of 330,000 g/mol would have a greater reduction of the T_g than the 10^6 g/mol linear polystyrene. Hence, these results suggest that, while the star-branched polymer behaves qualitatively like the linear polymer, quantitatively there is a possible difference that

requires further exploration by, e.g., running experiments on different star-branch molecular weight materials.

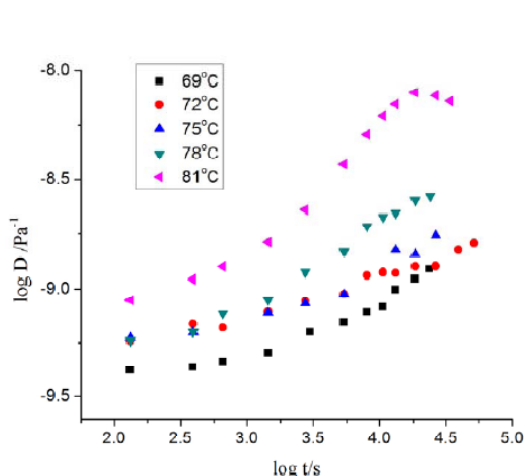


Figure 11. Creep compliance vs. logarithm of time for 28 nm thickness film of star-branched polystyrene at the temperatures indicated. (After ref. 13,15).

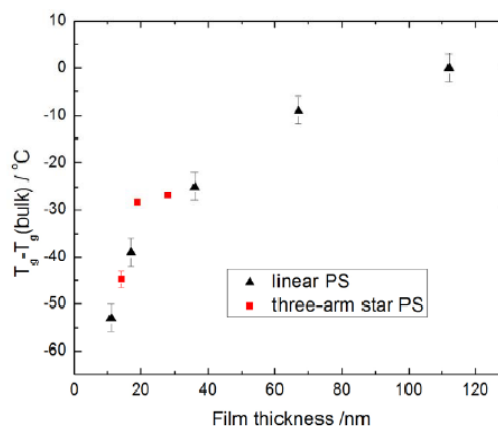


Figure 12. T_g reduction vs. film thickness linear and star-branched polystyrenes. (After ref.13,15).

Failure Behavior of Ultrathin Films

In the prior work we examined the viscoelastic properties of the ultrathin polystyrene. Here we look at the yield behavior of the polystyrene using the same type of films. In order to determine the behavior in a stress-strain test we applied stepped pressure histories according to the sequence shown in Figure 13. The time period for which the pressure steps were applied

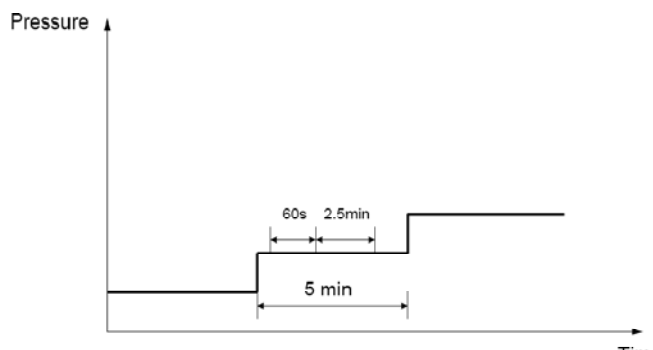


Figure 13. Schematic of pressure sequence for testing stress-strain to yield/failure of the bubbles. (After ref.13,15).

was 5 minutes. During that time, AFM scans were taken of the sample and images of the bubble obtained. For the scan rate of 2 Hz it takes approximately 2.5 minutes to complete the scan. For each loading step a duration of 60 s was used prior to scanning the sample. The pressure was increased in this fashion until bubble rupture occurred. Figure 14 shows the stress-strain behavior of 32 ± 1 nm films at different temperatures. At 26 °C, the film underwent uniform draw before rupture. At higher temperatures, the film yields and the yield stress decreases as

temperature increases. The strain at yield increases as temperature increases. Figure 15 shows the yield stress for the 32 nm thick films as a function of temperature. We see that the yield stress for these ultrathin films is smaller than what one would expect for a macroscopic glassy polymer where yield stresses tend to be near to 100 MPa. In addition, it is of interest to remark that the strains for yielding to occur are very small relative to what is observed macroscopically. Both these phenomena merit further investigation.

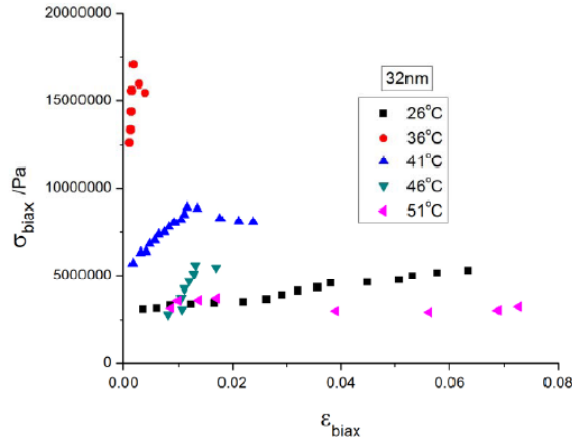


Figure 14. Biaxial stress-strain curves for a 32 nm thick polystyrene film at different temperatures as indicated. (After ref. 13).

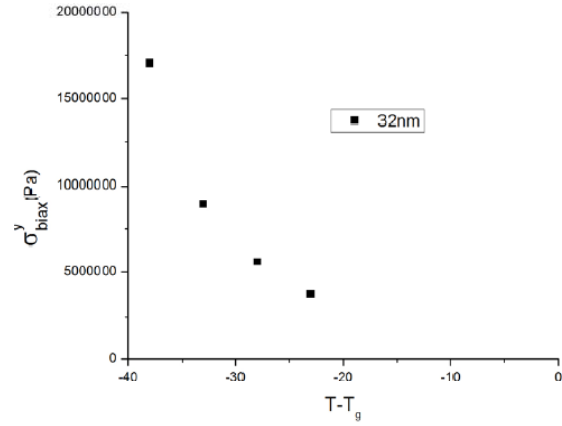


Figure 15. Biaxial yield stress vs distance below the glass transition temperature for a 32 nm thick polystyrene film (After ref. 13).

Bubble Inflation and Surface Tension of Ultrathin Films

One of the issues surrounding the behavior of the ultrathin polymer films is the possible surface tension effects on properties. In addition, because of the surface tension contributions to behavior, one might ask whether or not the surface tension of the ultrathin films can be determined from the bubble inflation measurements and, if so, does it change with film thickness? We were able to take two different routes to address these questions and in both instances we come to the conclusion that the surface tension, while contributing to the rubbery stiffening described above is not the cause of the rubbery stiffening. There is confinement induced stiffening in the ultrathin polymer films. In addition, we find that the surface tension is independent of the film thickness. To show this we present our results for the PBMA material.

If we plot $\frac{PR_0^2}{2\delta} + \frac{P\delta}{2}$ vs. $\frac{2.168Et\delta^2}{R_0^2}$, as shown in Figure 16, we can determine both the modulus of the film and its surface energy. This comes from the relationship for the energy contributions to the bubble inflation from surface energy and from the membrane stresses and the determining equation is¹¹:

$$\frac{PR_0^2}{2\delta} + \frac{P\delta}{2} = \frac{2.168Et\delta^2}{R_0^2} + 4\gamma$$

And δ is the bubble height, P is the internal pressure, R_0 is the radius of the bubble, E is the modulus and γ is the surface energy. From the slope we obtain E and from the intercept we obtain the surface energy. We have previously shown that the modulus (1/compliance) in the PBMA is stiffer for the thin films than in the bulk (see Figure 5). The surface energy determined from the intercept is shown in Figure 17. Here we see that, within the general uncertainty of the data, there is no film thickness effect on the film surface energy. We note that the data in Figures 5 and 17 are confirmed both by this analysis and by that in which stress-strain plots are used to obtain directly the modulus and the surface tension^{11,12}. The latter is included in Figure 17.

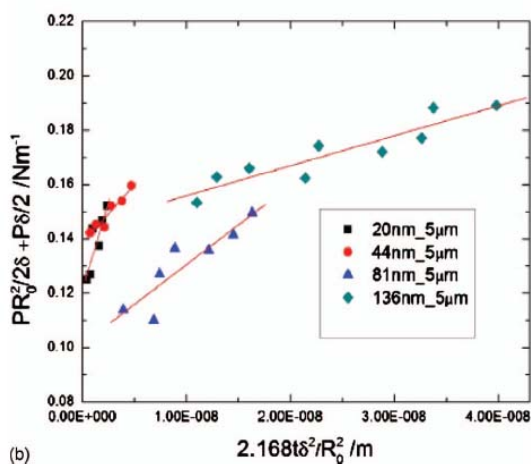


Figure 16. Energy balance plot for PBMA ultrathin films in the rubbery plateau regime. Slope gives modulus and intercept gives surface energy. (After ref.13).

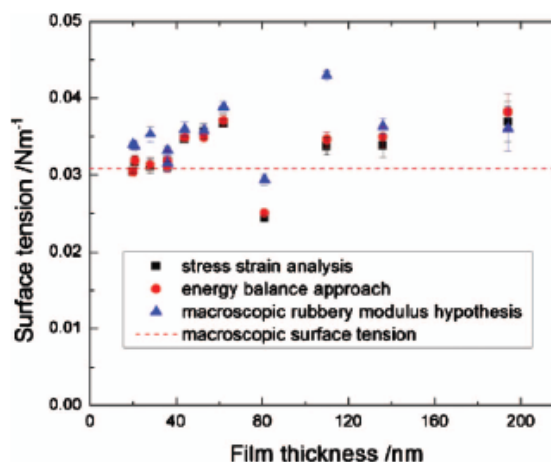


Figure 17. Surface tension vs. film thickness for PBMA films for stress-strain assumption, energy balance approach and macroscopic rubbery modulus assumption. (After ref.11).

Summary

Biaxial inflation of ultrathin polymer films has been used as a means to make nanomechanical measurements of the thermoviscoelastic response of a linear poly(vinyl acetate), a linear polystyrene, a star-branched polystyrene material, and a linear polycarbonate in the form of ultra thin films. Elastic data were obtained for poly(*n*-butyl methacrylate). The work has lead to several confirming results as well as to novel information concerning the property changes that ultrathin films undergo due to confinement or finite size effects. First, we have confirmed that the glass transition can decrease dramatically in the ultrathin films of polystyrene. Second, we have shown that the changes in T_g are non-universal, i.e., PVAc shows very little effect, polystyrene shows large effects and polycarbonate shows extremely large effects. In the case of the latter, 3 nm films show a T_g reduction of over 100 °C. We have also shown that the rubbery stiffening in the PS,PVAc and PC seems consistent in that the values for all three materials are similar and the compliance follows an approximately square dependence on film thickness. For the PBMA, on the other hand, the stiffening is less and seems to follow a sub-linear dependence on film thickness. We have also shown that the star-branched polystyrene of 330,000 g/mol molecular weight has similar behavior to the 10^6 molecular weight linear polystyrene.

In other work we have shown that the results are not significantly affected by the geometry of deformation, viz., equibiaxial as measured by the circular bubble inflation vs. plane strain as determined by the slotted geometry rectangular bubbles. Furthermore, we find that the yield stress and strain in the polystyrene seems to be dependent on the film thickness, being much reduced in this instance by going to 32 nm thickness. Finally, we have been able to show that the surface tension is not the cause of the observed stiffening and we find that the surface energy of the ultrathin films is consistent with that of the macroscopic material.

References

- ¹ P.A. O'Connell and G.B. McKenna, "Rheological Measurements of the Thermoviscoelastic Response of Ultrathin Polymer Films," *Science*, **307**, 1760-1763 (2005).
- ² P.A. O'Connell and G.B. McKenna, "Novel Nanobubble Inflation Method for Determining the Viscoelastic Properties of Ultrathin Polymer Films," *Rev. Sci. Instr.*, **78**, 013901-1 – 013901-12 (2007).
- ³ P.A. O'Connell, S.A. Hutcheson and G.B. McKenna, "Creep behavior of ultrathin polymer films," *Journal of Polymer Science. Part B. Polymer Physics Edition*, **46**, 1952-1965 (2008).
- ⁴ P.A. O'Connell and G.B. McKenna, "A novel nano-bubble inflation method for determining the viscoelastic properties of ultrathin polymer films," *Scanning*, **30**, 184-196 (2008).
- ⁵ M. Alcoutlabi and G.B. McKenna, "Effects of Confinement on Material Behaviour at the Nanometre Size Scale," *J. Phys.: Condensed Matter*, **17**, R461-R524 (2005).
- ⁶ K. Dalnoki-Veress, J.A. Forrest, P.G. de Gennes, J.R. Dutcher, "Glass transition reductions in thin freely-standing polymer films: A scaling analysis of chain confinement effects," *J. Physique IV*, **10**, 221-226 (2000).
- ⁷ K. Dalnoki-Veress, J.A. Forrest, C. Murray, C. Gigault and J.R. Dutcher, "Molecular weight dependence of reductions in the glass transition temperature of thin, freely standing polymer films," *Phys. Rev. E.*, **63**, 031801 (2001).
- ⁸ P.A. O'Connell, J. Wang and G.B. McKenna, "Exceptional Property Changes in Ultrathin Films of Polycarbonate : Glass temperature, rubbery stiffening and flow," manuscript in preparation.
- ⁹ P.A. O'Connell and G.B. McKenna, "Dramatic stiffening of ultrathin polymer films in the rubbery regime" *European Physical Journal E*, **20**, 143-150 (2006).
- ¹⁰ B. Nysten, C. Fretigny and S. Cuenot, "Elastic modulus of nanomaterials: resonant contact-AFM measurement and reduced-size effect," *Testing, Reliability, and Application of Micro-and Nano-Material Systems III*, ed. R. E. Geer, N. Meyendorf, G. Y. Baaklini, B. Michel, *Proceedings of SPIE Vol. 5766* (SPIE, Bellingham, WA, 2005) doi: 10.1117/12.604981
- ¹¹ S. Xu, P.A. O'Connell and G.B. McKenna, "Unusual elastic behavior of ultrathin polymer films: Confinement-induced/molecular stiffening and surface tension effects," *Journal of Chemical Physics*, **132**, 184902 (2010).
- ¹² P.A. O'Connell and G.B. McKenna, "The stiffening of ultrathin films in the rubbery regime: The relative contributions of membrane stress and surface tension," *J. Polymer Science. Part B. Polymer Physics*, **47**, 2441–2448 (2009).
- ¹³ S. Xu, *Mechanical Properties of Ultrathin Polymer Films Investigated by a Nanobubble Inflation Technique: Surface Tension, Geometry and Molecular Architecture Effects*, Ph.D. thesis, Department of Chemical Engineering, Texas Tech University, Lubbock, TX, USA, August, 2011.
- ¹⁴ S. Xu, P.A. O'Connell, G.B. McKenna and S. Castagnet, "Nanomechanical properties in ultrathin polymer films: Measurement on rectangular vs circular bubbles," *Journal of Polymer Science. Part B., Polymer Physics Edition*, submitted, October, 2011.
- ¹⁵ S. Xu and G.B. McKenna, "Nanomechanical response of ultrathin films of star-branched polystyrene," manuscript in preparation.